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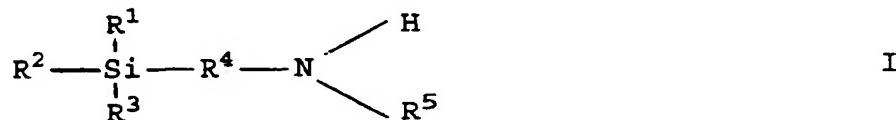
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(54) Aminosilane compounds in silica-filled rubber compositions

(57) The present invention relates to the use in a silica-filled rubber composition of an aminosilane compound of the formula



wherein R¹, R² and R³ are independently selected from the group consisting of alkoxy radicals having from 1 to 8 carbon atoms, alkyl radicals having 1 to 8 carbon atoms and aryl radicals having 6 carbon atoms, with the proviso that at least one of R¹, R² and R³ is an alkoxy radical; R⁴ is selected from the group consisting of alkylene groups having from 1 to 18 carbon atoms and arylene and alkyl substituted arylene groups having from 6 to 10 carbon atoms; R⁵ is selected from the group consisting of hydrogen and alkyl groups having from 1 to 15 carbon atoms.

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Description**Field of the Invention**

5 The present invention relates to the use in a silica-filled rubber composition of an aminosilane compound.

Background of the Invention

Sulfur-containing organosilicon compounds are useful as reactive coupling agents between rubber and silica fillers providing for improved physical properties. They are also useful as adhesion primers for glass, metals and other substrates.

U.S. Patent Nos. 3,842,111, 3,873,489 and 3,978,103 disclose the preparation of various sulfur-containing organosilicon compounds. These organosilicon compounds are commonly used in silica-reinforced rubber.

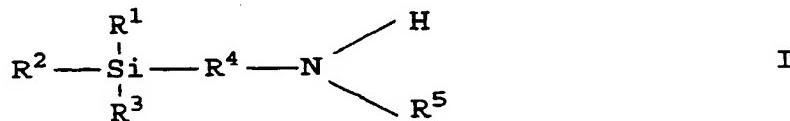
15 Summary of the Invention

The present invention relates to the use of an aminosilane compound in combination with a sulfur-containing organosilicon compound in a silica-filled rubber.

20 Detailed Description of the Invention

There is disclosed a method of processing a silica-filled rubber composition which comprises

- (i) 100 parts by weight of at least one sulfur-vulcanizable elastomer selected from conjugated diene homopolymers and copolymers and from copolymers of at least one conjugated diene and aromatic vinyl compound;
- 25 (ii) 10 to 250 phr of particulate precipitated silica;
- (iii) .05 to 10 phr of an aminosilane compound of the formula

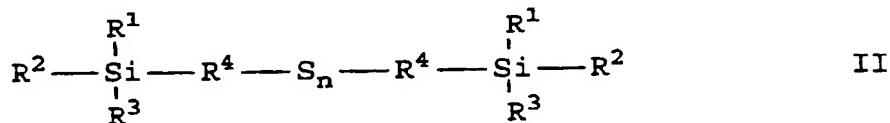


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wherein R¹, R² and R³ are independently selected from the group consisting of alkoxy radicals having from 1 to 8 carbon atoms, alkyl radicals having from 1 to 8 carbon atoms and aryl radicals having 6 carbon atoms, with the proviso that at least one of R¹, R² and R³ is an alkoxy radical; R⁴ is selected from the group consisting of alkylene groups having from 1 to 18 carbon atoms and arylene and alkyl-substituted arylene groups having from 6 to 10 carbon atoms; and R⁵ is selected from the group consisting of hydrogen and alkyl groups having from 1 to 15 carbon atoms; and

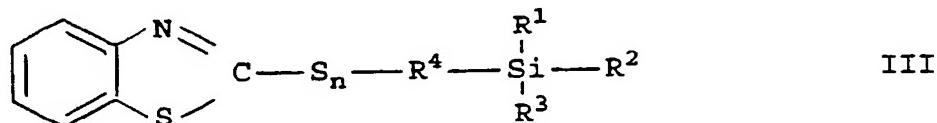
40 (iv) .05 to 10 phr of a sulfur-containing organosilicon compound of the formula:

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50 or

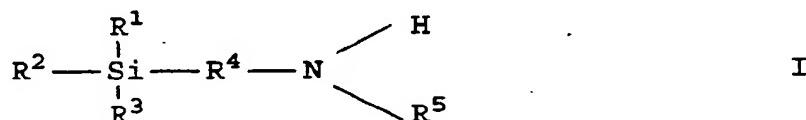
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wherein n is an integer of from 2 to 8.

There is disclosed a silica-filled rubber composition which comprises

- 5 (i) 100 parts by weight of at least one sulfur-vulcanizable elastomer selected from conjugated diene homopolymers and copolymers and from copolymers of at least one conjugated diene and aromatic vinyl compound;
- (ii) 10 to 250 phr of particulate precipitated silica;
- (iii) .05 to 10 phr of an aminosilane compound of the formula

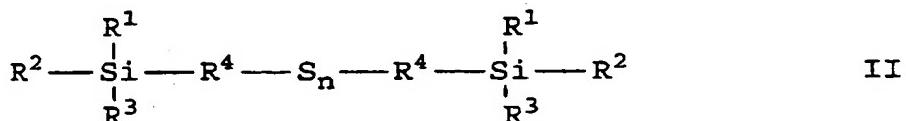


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wherein R¹, R² and R³ are independently selected from the group consisting of alkoxy radicals having from 1 to 8 carbon atoms, alkyl radicals having 1 to 8 carbon atoms and aryl radicals having 6 carbon atoms, with the proviso that at least one of R¹, R² and R³ is an alkoxy radical; R⁴ is selected from the group consisting of alkylene groups having from 1 to 18 carbon atoms and arylene and alkyl-substituted arylene groups having from 6 to 10 carbon atoms; and R⁵ is selected from the group consisting of hydrogen and alkyl groups having from 1 to 15 carbon atoms;

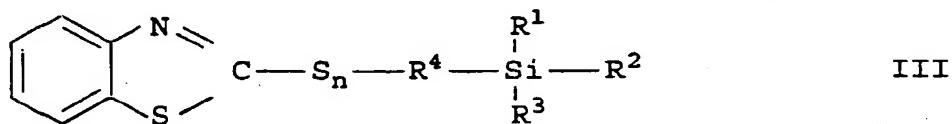
- (iv) .05 to 10 phr of a sulfur-containing organosilicon compound of the formula:

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or



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40 wherein n is an integer of from 2 to 8.

The present invention may be used with sulfur-vulcanizable rubbers or elastomers containing olefinic unsaturation. The phrase "rubber or elastomer-containing olefinic unsaturation" is intended to include both natural rubber and its various raw and reclaim forms as well as various synthetic rubbers. In the description of this invention, the terms "rubber" and "elastomer" may be used interchangeably, unless otherwise prescribed. The terms "rubber composition," "compounded rubber" and "rubber compound" are used interchangeably to refer to rubber which has been blended or mixed with various ingredients and materials and such terms are well known to those having skill in the rubber mixing or rubber compounding art. Representative synthetic polymers are the homopolymerization products of butadiene and its homologues and derivatives, for example, methylbutadiene, dimethylbutadiene and pentadiene as well as copolymers such as those formed from butadiene or its homologues or derivatives with other unsaturated monomers. Among the latter are acetylenes, for example, vinyl acetylene; olefins, for example, isobutylene, which copolymerizes with isoprene to form butyl rubber; vinyl compounds, for example, acrylic acid, acrylonitrile (which polymerize with butadiene to form NBR), methacrylic acid and styrene, the latter compound polymerizing with butadiene to form SBR, as well as vinyl esters and various unsaturated aldehydes, ketones and ethers; e.g., acrolein, methyl isopropenyl ketone and vinyl ethyl ether. Specific examples of synthetic rubbers include neoprene (polychloroprene), polybutadiene (including cis-1,4-polybutadiene), polyisoprene (including cis-1,4-polysisoprene), butyl rubber, styrene/isoprene/butadiene rubber, isoprene-butadiene copolymer, copolymers of 1,3-butadiene or isoprene with monomers such as styrene, acrylonitrile and methyl methacrylate, as well as ethylene/propylene terpolymers, also known as ethylene/propylene/diene monomer

(EPDM), and in particular, ethylene/propylene/dicyclopentadiene terpolymers and mixtures of the above. The preferred rubber or elastomers are polybutadiene and SBR.

In one aspect the rubber is at least two diene-based rubbers. For example, a combination of two or more rubbers is preferred such as cis 1,4-polyisoprene rubber (natural or synthetic, although natural is preferred), 3,4-polyisoprene rubber, styrene/isoprene/butadiene rubber, emulsion and solution polymerization derived styrene/butadiene rubbers, cis 1,4-polybutadiene rubbers and emulsion polymerization prepared butadiene/acrylonitrile copolymers.

In one aspect of this invention, an emulsion polymerization derived styrene/butadiene (E-SBR) might be used having a relatively conventional styrene content of about 20 to about 28 percent bound styrene or, for some applications, an E-SBR having a medium to relatively high bound styrene content; namely, a bound styrene content of about 30 to about 45 percent.

The relatively high styrene content of about 30 to about 45 for the E-SBR can be considered beneficial for a purpose of enhancing traction, or skid resistance, of the tire tread. The presence of the E-SBR itself is considered beneficial for a purpose of enhancing processability of the uncured elastomer composition mixture, especially in comparison to a utilization of a solution polymerization prepared SBR (S-SBR).

By emulsion polymerization prepared E-SBR, it is meant that styrene and 1,3-butadiene are copolymerized as an aqueous emulsion. Such are well known to those skilled in such art. The bound styrene content can vary, for example, from about 5 to about 50 percent. In one aspect, the E-SBR may also contain acrylonitrile to form a terpolymer rubber, as E-SBAR, in amounts, for example, of about 2 to about 30 weight percent bound acrylonitrile in the terpolymer.

Emulsion polymerization prepared styrene/butadiene/acrylonitrile copolymer rubbers containing about 2 to about 40 weight percent bound acrylonitrile in the copolymer are also contemplated as diene-based rubbers for use in this invention.

The solution polymerization prepared SBR (S-SBR) typically has a bound styrene content in a range of about 5 to about 50, preferably about 9 to about 36, percent. The S-SBR can be conveniently prepared, for example, by organo lithium catalyzation in the presence of an organic hydrocarbon solvent.

A purpose of using S-SBR is for improved tire rolling resistance as a result of lower hysteresis when it is used in a tire tread composition.

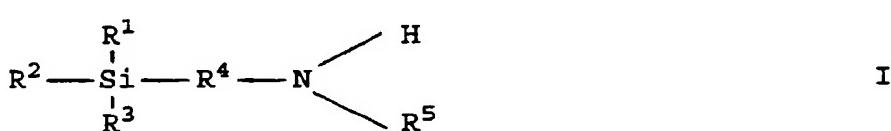
The 3,4-polyisoprene rubber (3,4-PI) is considered beneficial for a purpose of enhancing the tire's traction when it is used in a tire tread composition. The 3,4-PI and use thereof is more fully described in U.S. Patent No. 5,087,668 which is incorporated herein by reference. The Tg refers to the glass transition temperature which can conveniently be determined by a differential scanning calorimeter at a heating rate of 10°C per minute.

The cis 1,4-polybutadiene rubber (BR) is considered to be beneficial for a purpose of enhancing the tire tread's wear, or treadwear. Such BR can be prepared, for example, by organic solution polymerization of 1,3-butadiene. The BR may be conveniently characterized, for example, by having at least a 90 percent cis 1,4-content.

The cis 1,4-polyisoprene and cis 1,4-polyisoprene natural rubber are well known to those having skill in the rubber art.

The term "phr" as used herein, and according to conventional practice, refers to "parts by weight of a respective material per 100 parts by weight of rubber, or elastomer."

The aminosilane compounds used in the present invention are of the formula



wherein R¹, R² and R³ are independently selected from the group consisting of alkoxy radicals having from 1 to 8 carbon atoms, alkyl radicals having 1 to 8 carbon atoms and aryl radicals having 6 carbon atoms, with the proviso that at least one of R¹, R² and R³ is an alkoxy radical; R⁴ is selected from the group consisting of alkylene groups having from 1 to 18 carbon atoms and arylene and alkyl substituted arylene groups having from 6 to 10 carbon atoms; R⁵ is selected from the group consisting of hydrogen and alkyl groups having from 1 to 15 carbon atoms. Preferably, each R¹, R² and R³ are alkoxy radicals having from 1 to 3 carbon atoms, R⁴ is an alkylene group having from 1 to 3 carbon atoms and R⁵ is hydrogen. The aminosilane compounds may comprise a high purity product or mixture of aminosilane compounds conforming to the above formula I.

Representative of the aminosilane compounds include trimethoxysilyl ethyl amine, triethoxysilyl ethyl amine, tripropoxysilyl ethyl amine, tributoxysilyl ethyl amine, trimethoxysilyl propyl amine, triethoxysilyl propyl amine, tripropoxysilyl propyl amine, triisopropoxysilyl propyl amine, tributoxysilyl propyl amine, trimethoxysilyl butyl amine, triethoxysilyl butyl

amine, tripropoxysilyl butyl amine, tributoxysilyl butyl amine, trimethoxysilyl pentyl amine, triethoxysilyl pentyl amine, tripropoxysilyl pentyl amine, tributoxysilyl pentyl amine, trimethoxysilyl hexyl amine, triethoxysilyl hexyl amine, tripropoxysilyl hexyl amine, tributoxysilyl hexyl amine, trimethoxysilyl heptyl amine, triethoxysilyl heptyl amine, tripropoxysilyl heptyl amine, tributoxysilyl heptyl amine, trimethoxysilyl octyl amine, triethoxysilyl octyl amine, tripropoxysilyl octyl amine, tributoxysilyl octyl amine, and the like. Preferably, the aminosilane compound is triethoxysilyl propyl amine. Triethoxysilyl propyl amine is commercially available from Witco Corporation, OSi Specialties Group under the designation A-1100.

The aminosilane compounds used in the present invention may be added to the rubber by any conventional technique such as on a mill or in a Banbury. The amount of the aminosilane compound may vary widely depending on the type of rubber, the amount of sulfur-containing organosilane compound and other compounds present in the vulcanizable composition. Generally, the amount of the aminosilane compound is used in a range of from about .05 to about 10.0 phr with a range of .1 to about 5.0 phr being preferred. The aminosilane compound is preferably added in the non-productive stage with the silica and the sulfur-containing organosilicon coupling agent.

For ease in handling, the aminosilane compound may be used per se or may be deposited on suitable carriers. Examples of carriers which may be used in the present invention include silica, carbon black, alumina, alumina silicates, clay, kieselguhr, cellulose, silica gel and calcium silicate.

The rubber composition should contain a sufficient amount of silica, and carbon black, if used, to contribute a reasonably high modulus and high resistance to tear. The silica filler may be added in amounts ranging from 10 to 250 phr. Preferably, the silica is present in an amount ranging from 15 to 90 phr. If carbon black is also present, the amount of carbon black, if used, may vary. Generally speaking, the amount of carbon black will vary from 0 to 80 phr. Preferably, the amount of carbon black will range from 0 to 40 phr. It is to be appreciated that the sulfur-containing organosilicon compound may be used in conjunction with a carbon black, namely pre-mixed with a carbon black prior to addition to the rubber composition, and such carbon black is to be included in the aforesaid amount of carbon black for the rubber composition formulation.

Where the rubber composition contains both silica and carbon black, the weight ratio of silica to carbon black may vary. For example, the weight ratio may be as low as 1:5 to a silica to carbon black weight ratio of 30:1. Preferably, the weight ratio of silica to carbon black ranges from 1:3 to 20:1. The combined weight of the silica and carbon black, as herein referenced, may range from about 15 to about 100 phr, but is preferably from about 45 to about 90 phr.

The commonly employed siliceous pigments used in rubber compounding applications can be used as the silica in this invention, including pyrogenic and precipitated siliceous pigments (silica) and aluminosilicates, although precipitate silicas are preferred. The siliceous pigments preferably employed in this invention are precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate, e.g., sodium silicate.

Such silicas might be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of about 40 to about 600, and more usually in a range of about 50 to about 300 square meters per gram. The BET method of measuring surface area is described in the Journal of the American Chemical Society, Volume 60, page 304 (1930).

The silica may also be typically characterized by having a dibutylphthalate (DBP) absorption value in a range of about 100 to about 400, and more usually about 150 to about 300.

Further, the silica, as well as the aforesaid alumina and aluminosilicate may be expected to have a CTAB surface area in a range of about 100 to about 220. The CTAB surface area is the external surface area as evaluated by cetyl trimethylammonium bromide with a pH of 9. The method is described in ASTM D 3849 for set up and evaluation. The CTAB surface area is a well known means for characterization of silica.

Mercury surface area/porosity is the specific surface area determined by Mercury porosimetry. For such technique, mercury is penetrated into the pores of the sample after a thermal treatment to remove volatiles. Set-up conditions may be suitably described as using a 100 mg sample; removing volatiles during 2 hours at 105°C and ambient atmospheric pressure; ambient to 2000 bars pressure measuring range. Such evaluation may be performed according to the method described in Winslow, Shapiro in ASTM bulletin, p.39 (1959) or according to DIN 66133. For such an evaluation, a CARLO-ERBA Porosimeter 2000 might be used.

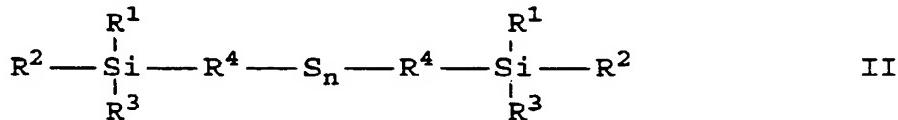
The average mercury porosity specific surface area for the silica should be in a range of about 100 to 300 m²/g. A suitable pore-size distribution for the silica, alumina and aluminosilicate according to such mercury porosity evaluation is considered herein to be 5 percent or less of its pores have a diameter of less than about 10 nm; 60 to 90 percent of its pores have a diameter of about 10 to about 100 nm; 10 to 30 percent of its pores have a diameter of about 100 to about 1000 nm; and 5 to 20 percent of its pores have a diameter of greater than about 1000 nm.

The silica might be expected to have an average ultimate particle size, for example, in the range of 0.01 to 0.05 micron as determined by the electron microscope, although the silica particles may be even smaller, or possibly larger, in size.

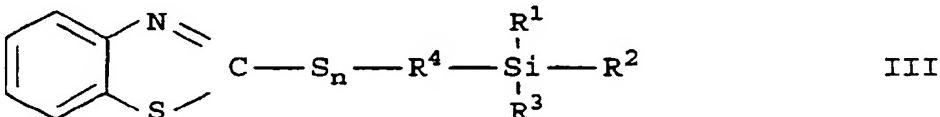
Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the Hi-Sil trademark with designations

210, 243, etc; silicas available from Rhone-Poulenc, with, for example, designations of Zeosil™ 1165MP and Z165GR and silicas available from Degussa AG with, for example, designations VN2, VN3, BV3380GR, etc, and silicas available from Huber, for example Huber Sil 8745.

The aminosilane compounds of formula I enhance the properties of the rubber when used in combination with a sulfur-containing organosilicon compounds. Examples of suitable sulfur-containing organosilicon compounds are of the formula:



or



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wherein n is an integer of from 2 to 8.

Specific examples of sulfur-containing organosilicon compounds of formula II which may be used in accordance with the present invention include: 3,3'-bis(trimethoxysilylpropyl) disulfide, 3,3'-bis(triethoxysilylpropyl) tetrasulfide, 3,3'-bis(triethoxysilylpropyl) octasulfide, 3,3'-bis(trimethoxysilylpropyl) tetrasulfide, 2,2'-bis(triethoxysilylethyl) tetrasulfide, 3,3'-bis(trimethoxysilylpropyl) trisulfide, 3,3'-bis(triethoxysilylpropyl) trisulfide, 3,3'-bis(tributoxysilylpropyl) disulfide, 3,3'-bis(trimethoxysilylpropyl) hexasulfide, 3,3'-bis(trimethoxysilylpropyl) octasulfide, 3,3'-bis(trioctoxysilylpropyl) tetrasulfide, 3,3'-bis(trihexoxysilylpropyl) disulfide, 3,3'-bis(tri-2'-ethylhexoxysilylpropyl) trisulfide, 3,3'-bis(triisooctoxysilylpropyl) tetrasulfide, 3,3'-bis(tri-t-butoxysilylpropyl) disulfide, 2,2'-bis(methoxy diethoxy silyl ethyl) tetrasulfide, 2,2'-bis(propoxysilylethyl) pentasulfide, bis(trimethoxysilylmethyl) tetrasulfide, 3-methoxy ethoxy propoxysilyl 3-diethoxybutoxysilylpropyltetrasulfide, 2,2'-bis(dimethyl methoxysilylethyl) disulfide, 2,2'-bis(dimethyl sec.butoxysilylethyl) trisulfide, 3,3'-bis(methyl butylethoxysilylpropyl) tetrasulfide, 3,3'-bis(di t-butylmethoxysilylpropyl) tetrasulfide, 2,2'-bis(phenyl methyl methoxysilylethyl) trisulfide, 3,3'-bis(diphenyl isopropoxysilylpropyl) tetrasulfide, 3,3'-bis(dimethyl ethylmercaptosilylpropyl) tetrasulfide, 2,2'-bis(methyl dimethoxysilylethyl) trisulfide, 2,2'-bis(methyl ethoxypropoxysilylethyl) tetrasulfide, 3,3'-bis(diethyl methoxysilylpropyl) tetrasulfide, 3,3'-bis(ethyl di-sec. butoxysilylpropyl) disulfide, 3,3'-bis(propyl diethoxysilylpropyl) disulfide, 3,3'-bis(butyl dimethoxysilylpropyl) trisulfide, 3,3'-bis(phenyl dimethoxysilylpropyl) tetrasulfide, 3-phenyl ethoxybutoxysilyl 3-trimethoxysilylpropyl tetrasulfide, 4,4'-bis(trimethoxysilylbutyl) tetrasulfide, 6,6'-bis(triethoxysilylhexyl) tetrasulfide, 12,12'-bis(triisopropoxysilyl dodecyl) disulfide, 18,18'-bis(trimethoxysilyloctadecyl) tetrasulfide, 18,18'-bis(tripropoxysilyloctadecenyl) tetrasulfide, 4,4'-bis(trimethoxysilylbuten-2-yl) tetrasulfide, 4,4'-bis(trimethoxysilylcyclohexylene) tetrasulfide, 5,5'-bis(dimethoxymethylsilylpentyl) trisulfide, 3,3'-bis(trimethoxysilyl-2-methylpropyl) tetrasulfide, 3,3'-bis(dimethoxyphenylsilyl-2-methylpropyl) disulfide.

The preferred sulfur-containing organosilicon compounds of formula II are the 3,3'-bis(trimethoxy or triethoxy silylpropyl) sulfides. The most preferred compounds are 3,3'-bis(triethoxysilylpropyl) tetrasulfide and 3,3'-bis(triethoxysilylpropyl) disulfide.

45 Representative sulfur-containing organosilicon compounds of formula III which may be used in accordance with the present invention include 2-benzothiazyl-(3-triethoxysilylpropyl) disulfide; 2-benzothiazyl-(2-trimethoxysilylethyl) disulfide; 2-benzothiazyl-(3-trimethoxysilylpropyl) disulfide; 2-benzothiazyl-(2-triethoxysilylpropyl) disulfide; 2-benzothiazyl-(2-tripropoxysilylethyl) disulfide; 2-benzothiazyl-(2-tri-sec-butoxysilylethyl) disulfide; 2-benzothiazyl-(2-tri-t-butoxysilylethyl) disulfide; 2-benzothiazyl-(3-triisopropoxysilylpropyl) disulfide; 2-benzothiazyl-(3-trioctoxysilylpropyl) disulfide; 2-benzothiazyl-(2-2'-ethylhexoxysilylethyl) disulfide; 2-benzothiazyl-(2-dimethoxy ethoxysilylethyl) disulfide; 2-benzothiazyl-(3-methoxyethoxypropoxysilylpropyl) disulfide; 2-benzothiazyl-(3-dimethoxymethylsilylpropyl) disulfide; 2-benzothiazyl-(3-methoxy dimethylsilylpropyl) disulfide; 2-benzothiazyl-(3-diethoxymethylsilylpropyl) disulfide; 2-benzothiazyl-(3-ethoxydimethylsilylpropyl) disulfide; 2-benzothiazyl-(4-trimethoxysilylbutyl) disulfide; 2-benzothiazyl-(3-dimethoxy methylsilyl-3-ethylpropyl) disulfide; 2-benzothiazyl-(3-tripropoxysilyl-3-methylpropyl) disulfide; 2-benzothiazyl-(3-dimethoxy phenylsilyl-2-methylpropyl) disulfide; 2-benzothiazyl-(12-trimethoxysilyldodecyl) disulfide; 2-benzothiazyl-(18-methoxydimethylsilyloctadecyl) disulfide; 2-benzothiazyl-(2-trimethoxysilyl-2-methylethyl) disulfide; 2-benzothiazyl-(2-

5 tripropoxysilyl-2-methylethyl) disulfide; 2-benzothiazyl-(2-trioctoxysilyl-2-methylethyl) disulfide; 2-benzothiazyl-(2-tri-methoxysilyl-phenyl) disulfide; 2-benzothiazyl-(2-triethoxysilyl-phenyl) disulfide; 2-benzothiazyl-(2-trimethoxysilyl-tolyl) disulfide; 2-benzothiazyl-(2-triethoxysilyl-tolyl) disulfide; 2-benzothiazyl-(2-trimethoxysilyl-methyl tolyl) disulfide; 2-benzothiazyl-(2-triethoxysilyl-methyl tolyl) disulfide; 2-benzothiazyl-(2-trimethoxysilyl-ethyl phenyl) disulfide; 2-benzothiazyl-(2-triethoxysilyl-ethyl phenyl) disulfide; 2-benzothiazyl-(2-trimethoxysilyl-ethyl tolyl) disulfide; 2-benzothiazyl-(3-trimethoxysilyl-propyl phenyl) disulfide; 2-benzothiazyl-(3-triethoxysilyl-propyl phenyl) disulfide; 2-benzothiazyl-(3-trimethoxysilyl-propyl tolyl) disulfide; and 2-benzothiazyl-(3-triethoxysilyl-propyl tolyl) disulfide.

10 The amount of the above sulfur-containing organosilicon compound in a rubber composition will vary depending on the level of silica that is used. Generally speaking, the amount of the compound of formula II or formula III will range from .05 to 10.0 phr. Preferably, the amount will range from .1 to 8 phr. Mixtures of the sulfur-containing organosilicon compounds of formula II and III may also be used.

15 In accordance with one aspect of this invention, a rubber composition is prepared by a process which comprises the sequential steps of:

- (A) thermomechanically mixing in at least one preparatory mixing step to a temperature of about 140°C to about 190°C, for a total mixing time of about 2 to about 20 minutes (i) 100 parts by weight of at least one sulfur-vulcanizable elastomer selected from conjugated diene homopolymers and copolymers and copolymers of at least one conjugated diene and aromatic vinyl compound; (ii) about 15 to about 100 phr of particulate filler selected from the group consisting of precipitated silica, alumina, aluminosilicate, carbon black and mixtures thereof; (iii) about 0.001 to about 0.10 parts by weight per part by weight of said particulate filler of at least one aminosilane compound of formula I; and (iv) about 0.03 to about 0.20 parts by weight per part by weight of said particulate filler of a sulfur-containing organosilicon compound of formula II, formula III or mixtures thereof;
- (B) subsequently blending therewith, in a final thermomechanical mixing step at a temperature to about 100°C to about 130°C for a time of about 1 to about 3 minutes, about 0.4 to about 3 phr of elemental sulfur provided, however, that the total free sulfur available from said sulfur donor addition introduced in said preparatory mixing steps and elemental sulfur added in said final mixing step is in a range of about 0.45 to about 5 phr.

It is readily understood by those having skill in the art that the rubber composition would be compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable constituent rubbers with various commonly used additive materials such as, for example, sulfur donors, curing aids, such as activators and retarders and processing additives, such as oils, resins including tackifying resins and plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants and peptizing agents. As known to those skilled in the art, depending on the intended use of the sulfur-vulcanizable and sulfur-vulcanized material (rubbers), the additives mentioned above are selected and commonly used in conventional amounts. Typical amounts of reinforcing-type carbon blacks(s), for this invention, if used, are herein set forth. Representative examples of sulfur donors include elemental sulfur (free sulfur), an amine disulfide, polymeric polysulfide and sulfur olefin adducts. Preferably, the sulfur-vulcanizing agent is elemental sulfur. The sulfur-vulcanizing agent may be used in an amount ranging from 0.5 to 8 phr, with a range of from 1.5 to 6 phr being preferred. Typical amounts of tackifier resins, if used, comprise about 0.5 to about 10 phr, usually about 1 to about 5 phr. Typical amounts of processing aids comprise about 1 to about 50 phr. Such processing aids can include, for example, aromatic, napthenic, and/or paraffinic processing oils. Typical amounts of antioxidants comprise about 1 to about 5 phr. Representative antioxidants may be, for example, diphenyl-p-phenylenediamine and others, such as, for example, those disclosed in the Vanderbilt Rubber Handbook (1978), pages 344-346. Typical amounts of antiozonants comprise about 1 to 5 phr. Typical amounts of fatty acids, if used, which can include stearic acid, comprise about 0.5 to about 3 phr. Typical amounts of zinc oxide comprise about 2 to about 5 phr. Typical amounts of waxes comprise about 1 to about 5 phr. Often microcrystalline waxes are used. Typical amounts of peptizers comprise about 0.1 to about 1 phr. Typical peptizers may be, for example, pentachlorothiophenol and dibenzamidodiphenyl disulfide.

In one aspect of the present invention, the sulfur-vulcanizable rubber composition is then sulfur-cured or vulcanized.

50 Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment, a single accelerator system may be used; i.e., primary accelerator. The primary accelerator(s) may be used in total amounts ranging from about 0.5 to about 4, preferably about 0.8 to about 2.0, phr. In another embodiment, combinations of a primary and a secondary accelerator might be used with the secondary accelerator being used in a smaller, equal or greater amount to the primary accelerator. Combinations of these accelerators might be expected to produce a synergistic effect on the final properties and are somewhat better than those produced by use of either accelerator alone. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures but produce a satisfactory cure at ordinary vulcanization temperatures. Vulcanization retarders might also be used. Suitable types of accelerators that may be used in the present invention are

amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound.

The mixing of the rubber composition can be accomplished by methods known to those having skill in the rubber mixing art. For example, the ingredients are typically mixed in at least two stages, namely at least one non-productive stage followed by a productive mix stage. The final curatives including sulfur-vulcanizing agents are typically mixed in the final stage which is conventionally called the "productive" mix stage in which the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) than the preceding non-productive mix stage(s). The rubber, silica, the combination of the aminosilane and the sulfur-containing organosilicon compound and carbon black, if used, are mixed in one or more non-productive mix stages. The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art. The non-productive sulfur-vulcanizable rubber composition containing the aminosilane of formula I, vulcanizable rubber and generally at least part of the silica, as well as the sulfur-containing organosilicon compound, may be subjected to a thermomechanical mixing step. The thermomechanical mixing step generally comprises a mechanical working in a mixer or extruder for an extended period of time at a rubber temperature between 140°C and 190°C. The appropriate duration of the thermomechanical working varies as a function of the operating conditions and the volume and nature of the components and the final properties of the compounded rubber desired. For example, the thermomechanical working may be from 1 to 20 minutes.

In one aspect of the invention, such process is provided wherein said preparatory mixing is conducted with at least two thermomechanical mixing steps to a temperature in a range of about 140°C to about 190°C, with intermediate cooling of the rubber composition between at least two of said mixing steps to a temperature below about 50°C.

In further accordance with the invention, the process comprises the additional step of vulcanizing the prepared rubber composition at a temperature in a range of about 100°C to about 200°C.

Accordingly, the invention also thereby contemplates a vulcanized rubber composition prepared by such process.

In additional accordance with the invention, the process comprises the additional steps of preparing an assembly 25 of a tire or sulfur-vulcanizable rubber with a tread comprised of the said rubber composition prepared according to the process of this invention and vulcanizing the assembly at a temperature in a range of about 100°C to about 200°C.

Accordingly, the invention also thereby contemplates a vulcanized tire prepared by such process.

Vulcanization of the rubber composition of the present invention is generally carried out at conventional temperatures ranging from about 100°C to 200°C. Preferably, the vulcanization is conducted at temperatures ranging from about 110°C to 180°C. Any of the usual vulcanization processes may be used such as heating in a press or mold, heating with superheated steam or hot air or in a salt bath.

Upon vulcanization of the sulfur-vulcanized composition, the rubber composition of this invention can be used for various purposes. For example, the sulfur-vulcanized rubber composition may be in the form of a tire, belt or hose. In case of a tire, it can be used for various tire components. Such tires can be built, shaped, molded and cured by various methods which are known and will be readily apparent to those having skill in such art. Preferably, the rubber composition is used in the tread of a tire. As can be appreciated, the tire may be a passenger tire, aircraft tire, truck tire and the like. Preferably, the tire is a passenger tire. The tire may also be a radial or bias, with a radial tire being preferred.

Example 1

40 In this example, triethoxysilyl propyl amine is evaluated in combination with various sulfur-containing organosilicon compounds. Rubber compositions containing the materials set out in Table 1 and 2 were prepared in a Kobe™ mixer using two separate stages of addition (mixing); namely, one non-productive mix stage and one productive mix stage. The total mixing time for the nonproductive was eight minutes including five minutes at a rubber temperature of 160°C. An initial three minutes were required to raise the stock temperature to 160°C. The total mixing time for the productive was two minutes to a rubber temperature below 120°C. The aminosilane and various sulfur-containing organosilicon compounds, accelerator and sulfur are listed as being "variable" in Table 1 and are more specifically set forth in Table 2.

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Table 1

Non-Productive	
5	SBR Rubber ¹
10	Polybutadiene ²
15	Natural Rubber
20	Isoprene/Butadiene Copolymer ³
25	Silica ⁴
30	Carbon Black
	Processing Oil and Wax
	Zinc Oxide
	Fatty Acid
	Antidegradant ⁵
	Triethoxysilyl propyl amine ⁶
	Si69 ⁷
	bis-(3-triethoxysilylpropyl)disulfide
	2-Benzothiazyl-(3-triethoxysilyl) propyl disulfide
Productive	
	N-cyclohexyl benzothiazole-2-sulfenamide
	Diphenyl guanidine
	sulfur

¹emulsion polymerized styrene/butadiene copolymer rubber with 40 percent by weight bound styrene. The rubber composed of 100 parts by weight rubber and 37.5 parts by weight aromatic oil and was obtained from The Goodyear Tire & Rubber Company

²cis 1,4-polybutadiene rubber from The Goodyear Tire & Rubber Company under designation Budene® 1207

³copolymer of isoprene and butadiene containing 50 percent by weight isoprene and 50 percent by weight butadiene having a glass transition temperature (Tg) of -45°C and was obtained from The Goodyear Tire & Rubber Company

⁴Zeosil™ MP1165

⁵N-1,3-dimethyl butyl, N'-phenyl paraphenylen diamine

⁶A-1100

⁷obtained as bis-(3-triethoxysilylpropyl) tetrasulfide, commercially available as X50S from Degussa AG which is provided in a 50/50 blend with carbon black and, thus, considered as being 50 percent active when the blend is considered. The phr reported in Table 2 is based on an active bis (3-triethoxysilylpropyl)tetrasulfide.

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Table 2

Samples	Ctrl 1	2	Ctrl 3	4	Ctrl 5	6	Ctrl 7	8	9
5 Triethoxysilyl propyl amine	0	0.5	0	0.5	0.0	0.5	0	1.0	2.0
10 Si69	6.4	6.4	0	0	0	0	0	0	0
15 bis-(3-triethoxysilylpropyl) disulfide	0	0	0	0	8.0	8.0	6.0	5.0	6.0
20 2-Benzothiazyl-(3-triethoxysilyl) propyldisulfide	0	0	7.0	7.0	0	0	0	0	0
25 N-cyclohexyl benzothiazole-2-sulfenamide	1.7	1.7	0.4	0.4	1.7	1.7	1.7	1.7	1.7
30 Sulfur	1.4	1.4	1.4	1.4	2.16	2.16	2.16	2.16	2.16
Stress Strain									
M100, MPa	2.29	2.42	2.58	2.67	3.08	3.18	2.41	2.33	2.59
M300, MPa	10.20	11.12	11.82	12.04	11.17	11.83	9.32	9.77	11.10
M300/M100	4.45	4.60	4.58	4.51	3.63	3.72	3.87	4.19	4.29
Rebound									
Room Temperature	36	37	38	39	31	32	34	35	35
100°C	59	60	61	60	57	58	56	56	55
DIN Abrasion Resistance ¹ (relative weight loss)	105	98	94	88	108	107	116	111	106

¹According to DIN 53516.

The rubber compositions of this example are identified herein as Samples 1-9. Samples 1, 3, 5 and 7 are considered herein as being controls without the use of an aminosilane added during the nonproductive stage. Thus, sample 2 is to be compared to control sample 1, sample 4 is to be compared to control sample 3, sample 6 is to be compared to control sample 5 and samples 8 and 9 are to be compared to control sample 7. The samples were cured at 150°C for 18 minutes.

Table 2 illustrates the behavior and physical properties of the cured samples 1-9. It is clearly evident that, when an aminosilane is used in combination with a sulfur-containing organosilicon compound, higher modulus values are obtained as well as greater M300/M100 ratios. The additional presence of the aminosilane also lowers the abrasion weight-loss values.

These physical property changes upon addition of aminosilane in addition to or in partial replacement of the sulfur-containing organosilicon compound are predictive of greater strength and abrasion resistance performance for the cured rubber compositions. Such compositions would be expected to provide improved treadwear when used as tire treads.

In addition, it is also evident that, when an aminosilane is used in combination with a sulfur-containing organosilicon compound, higher rebound values are obtained. This is predictive of reduced hysteresis for the cured rubber composition. Such compositions would be expected to provide improved (reduced) rolling resistance when used as tire treads.

The combined beneficial tendencies to improved abrasion resistance and hysteresis provided by the combination of an aminosilane and a sulfur-containing organosilicon compound to a silica-filled rubber composition are very desirable.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

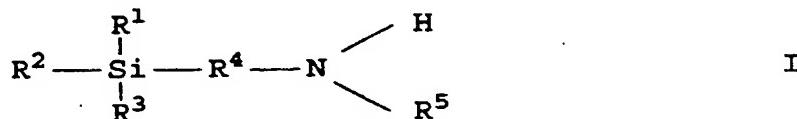
Claims

1. A method of processing a silica-filled rubber composition which comprises mixing

5 (i) 100 parts by weight of at least one sulfur-vulcanizable elastomer selected from conjugated diene homopolymers and copolymers and from copolymers of at least one conjugated diene and aromatic vinyl compound;

 (ii) 10 to 250 phr of particulate precipitated silica;

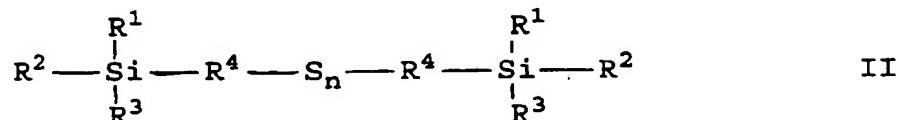
 (iii) .05 to 10 phr of an aminosilane compound of the formula



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wherein R¹, R² and R³ are independently selected from the group consisting of alkoxy radicals having from 1 to 8 carbon atoms, alkyl radicals having 1 to 8 carbon atoms and aryl radicals having 6 carbon atoms, with the proviso that at least one of R¹, R² and R³ is an alkoxy radical; R⁴ is selected from the group consisting of alkylene groups having from 1 to 18 carbon atoms and arylene and alkyl-substituted arylene groups having from 6 to 10 carbon atoms; and R⁵ is selected from the group consisting of hydrogen and alkyl groups having from 1 to 15 carbon atoms; and

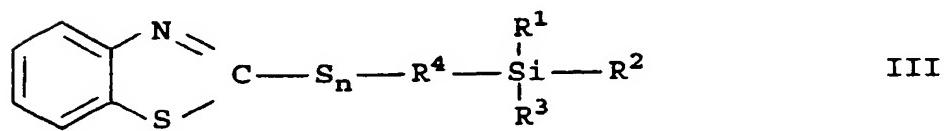
(iv) .05 to 10 phr of a sulfur-containing organosilicon compound of the formula:



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or



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wherein n is an integer of from 2 to 8.

- 45 2. The method of claim 1 characterized in that each R¹, R² and R³ are alkoxy radicals having 1 to 3 carbon atoms, R⁴ is an alkylene group having 1 to 3 carbon atoms and R⁵ is hydrogen.

3. The method of any preceding claim wherein said silica-filled rubber composition is thermomechanically mixed at a rubber temperature in a range of from 140°C to 190°C for a mixing time of from 1 to 20 minutes.

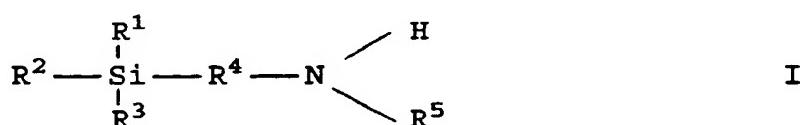
50 4. The method of any preceding claim including the sequential steps of:

(A) thermomechanically mixing in at least one preparatory mixing step to a temperature of about 140°C to about 190°C for a total mixing time of about 2 to about 20 minutes (i) 100 parts by weight of at least one sulfur-vulcanizable elastomer selected from conjugated diene homopolymers and copolymers and copolymers of at least one conjugated diene and aromatic vinyl compound; (ii) about 15 to about 100 phr of particulate filler selected from the group consisting of precipitated silica, alumina, aluminosilicate, carbon black and mixtures thereof; (iii) about 0.05 to about 10 parts by weight per part by weight of said particulate filler of an aminosilane

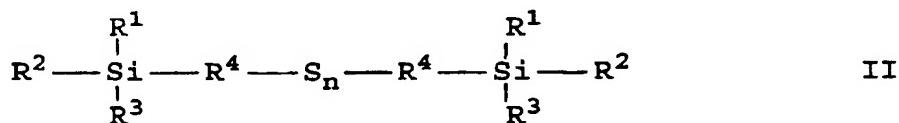
compound of formula I; and (iv) about 0.05 to about 20 parts by weight per part by weight of said particulate filler of a sulfur-containing organosilicon compound of formula II, formula III or mixtures thereof; and
 5 (B) subsequently blending therewith, in a final thermomechanical mixing step at a temperature to about 100°C to about 130°C for a time of about 1 to about 3 minutes, about 0.4 to about 3 phr of elemental sulfur provided, however that the total of free sulfur introduced in said preparatory mixing steps and elemental sulfur added in said final mixing step is in a range of about 0.45 to about 5 phr.

5. A silica-filled rubber composition which is characterized by

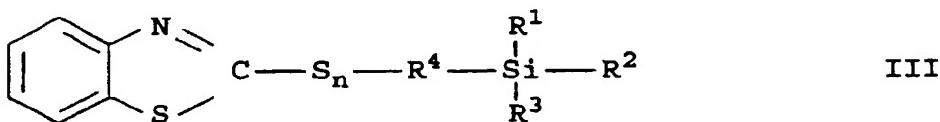
- 10 (i) 100 parts by weight of at least one sulfur-vulcanizable elastomer selected from conjugated diene homopolymers and copolymers and from copolymers of at least one conjugated diene and aromatic vinyl compound;
 (ii) 10 to 250 phr of particulate precipitated silica;
 (iii) .05 to 10 phr of an aminosilane compound of the formula



20 wherein R¹, R² and R³ are independently selected from the group consisting of alkoxy radicals having from 1 to 8 carbon atoms; R⁴ is selected from the group consisting of alkylene groups having from 1 to 18 carbon atoms and arylene and alkyl-substituted arylene groups having from 6 to 10 carbon atoms; and R⁵ is selected from the group consisting of hydrogen and alkyl groups having from 1 to 15 carbon atoms; and
 25 (iv) .05 to 10 phr of a sulfur-containing organosilicon compound of the formula:



or



40 wherein n is an integer of from 2 to 8.

- 45 6. The composition of claim 5 characterized in that each R¹, R² and R³ are alkoxy radicals having 1 to 3 carbon atoms, R⁴ is an alkylene group having 1 to 3 carbon atoms and R⁵ is hydrogen.
 7. The composition of claims 5 and 6 characterized in that said composition was thermomechanically mixed at a rubber temperature in a range of from 140°C to 190°C for a total mixing time of from 1 to 20 minutes.
 50 8. A sulfur-vulcanized rubber composition which is characterized by being prepared by heating the composition of claims 5, 6 and 7 to a temperature ranging from 100°C to 200°C in the presence of a sulfur-vulcanizing agent.
 9. The sulfur-vulcanized rubber composition of claim 8 characterized in that said composition is in the form of a tire, belt or hose.
 55 10. A tire having a tread characterized by the composition of claim 8.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 97 10 9827

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X,P	EP 0 767 206 A (MICHELIN & CIE) 9 April 1997 * abstract; claims; examples 2,3 * ---	1-10	C08K5/54 C08L21/00
A	US RE30450 E (IANNICELLI) 16 December 1980 * abstract; claims; tables *		
A	DE 43 08 311 A (DEGUSSA) 22 September 1994 * examples 4-3 *		
A	G.GODLEWSKA ET AL.: "ESTIMATION OF THE EFFECT OF SURFACE MODIFICATION OF" INTERNATIONAL POLYMER SCIENCE AND TECHNOLOGY., vol. 6, 1979, SHAWBURY GB, pages T61-T64, XP002042004 * page T64, last paragraph; tables 2-4 * -----		
TECHNICAL FIELDS SEARCHED (Int.Cl.6)			
C08K			
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search		Examiner
THE HAGUE	1 October 1997		Mettler, R-M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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